

Project Number: 86759 (renewed from former project 70179)

Project Title: Radionuclide Sensors for Water Monitoring

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Number of Graduate Students Actively Involved in the Project: 2

Number of Undergraduate Students Involved (part-time) in the Project: 1

Number of Post-Doctoral Scholars Involved (part-time) in the Project: 2

Number of Ph.D. degrees granted involved in the Project: 0

Number of M.S. degrees granted involved in the Project: 0

Research Objective

Radionuclide contamination in the soil and groundwater at U.S. Department of Energy (DOE) sites is a severe problem that requires monitoring and remediation. Radionuclide measurement techniques are needed to monitor surface waters, groundwater, and process waters. Typically, water samples are collected and transported to an analytical laboratory, where costly radiochemical analyses are performed. To date, there has been very little development of selective radionuclide sensors for alpha- and beta-emitting radionuclides such as ^{90}Sr , ^{99}Tc , and various actinides of interest.

The objective of this project is to develop and investigate novel sensor concepts and materials for sensitive and selective determination of beta- and alpha-emitting radionuclide contaminants in water. To meet the requirements for low-level, isotope-specific detection, the proposed sensors are based on radiometric detection. As a means to address the fundamental challenge of the short ranges of beta and alpha particles in water, our overall approach is based on localization of preconcentration/separation chemistries directly on or within the active area of a radioactivity detector. Of specific interest is the development of robust, reagentless sensor systems suitable for implementation in the in-situ sensor probe devices for monitoring of the difficult to detect radionuclides.

The outcome of these investigations will be the knowledge necessary to choose appropriate chemistries for selective preconcentration of radionuclides from environmental samples, new

materials that combine chemical selectivity with scintillating properties, new materials that add chemical selectivity to solid-state diode detectors, new preconcentrating column sensors, and improved instrumentation and signal processing for selective radionuclide sensors. New knowledge will provide the basis for designing effective probes and instrumentation for field and in situ measurements.

Research Progress and Implications

This report summarizes work after 3 years of the renewed 3 year program. The research effort is being directed at the investigation of the reagentless equilibration sensing concept for the purpose of ^{99}Tc in situ sensing, development of the equilibration sensing theory, characterization of the sorbent and sensor materials, investigation of the chemically modified diode detection, development and modeling of the scintillation and diode detection systems, and digital signal processing.

The preconcentrating column sensor concept is based on the use of dual function materials that enable selective sorbent and scintillating properties attained within the sensor column. The quantification method is based on achieving complete sensor equilibrium with the sample solution, at which point no further preconcentration occurs, and the analyte concentration on the sensor is proportional to the analyte concentration in the sample. Because the sensor re-equilibrates with the next sample, no sensor regeneration is necessary. This forms the basis for reagentless operation, which is well suited for the development of long term in situ probes. Challenges and scientific issues associated with this novel sensing approach are one of the key areas of this research program. Development of the theoretical model that enables prediction of the key operational parameters of the sensor system (retention volume, equilibration volume, detection and chromatographic efficiency) are of particular significance

We have completed systematic evaluation of the sorbent and scintillator materials and sensor configurations for use in equilibrium ^{99}Tc sensing in groundwater. Our studies continue to indicate that weakly basic anion exchange materials are preferred due to better resistance towards fouling by dissolved natural organic matter (e.g. humic acids). We have completed systematic studies of the guard column materials that can be used to remove humic acids without capturing pertechnetate.

We have completed detailed evaluation of the equilibration sensing approach using mixed bed microcolumn geometry optimization of the sorbent-to-scintillator ratios. The equilibration sensing theory has been developed in detail and model predictions are in excellent agreement with the experiment. Effects of the stable and radioactive interferences in the analysis of ground water samples have been characterized in detail. Approaches towards mitigating effects of interfering species have been developed and demonstrated. The feasibility of accurate ^{99}Tc equilibration sensing below regulatory levels in actual Hanford groundwater has been demonstrated with several well water samples. The testing was conducted using both laboratory and prototypical field instrumentation developed in collaboration with Advanced Monitoring System Initiative. The results indicate that this sensor concept is offering a revolutionary capability in designing practical sensor probes suitable for in situ, reagentless detection.

The research has continued in the area of chemically modified diode detectors. We have completed systematic evaluation of the thin film uptake properties for actinides using several extractants and plasticizers. Moreover, the research has been expanded to the use of semiconductor diode detectors for analysis of Tc in liquid samples. Strongly basic anion exchange material was used to capture and localize ^{99}Tc in a close proximity to the detector surface. The experiments were conducted both in a batch and flow regime. The feasibility of sensitive quantification using fountain flow cell for sample delivery has been demonstrated.

In addition to using chemically modified diode detectors, we have conducted studies on using thin film coated scintillator detectors for detection of alpha emitting radionuclides in aqueous samples.

Planned activities

The most significant outcome of this program was the development of equilibration-based sensing theory and practices for selective detection of low levels of radionuclide contaminants in water. This breakthrough development opened for the first time the possibility of designing practical sensor probes for reagentless, long term in-situ monitoring of water samples. The research has progressed from basic experimental and theoretical studies to the development of the prototype systems of significant potential for use at the contaminated sites. It is our hope that the opportunity to continue this research effort will present itself in the future. Continuation of this research will lead to the development of unique practical sensor system for analysis of major radioactive contaminants at the US DOE sites.

Information Access

- Egorov O.B, O'Hara M.J, Grate J.W, Knopf M.A., Anderson G., Hartman J.S. "Radiochemical Sensor System for the Analysis of ^{99}Tc (VII) in Groundwater." *J. Radioanal. & Nucl. Chem.*, **2005**, Vol. 264, No. 2, 495-500
- J. W. Grate, O.B. Egorov, and M.J. O'Hara, "Sensors and Automated Analyzers for Radionuclides, in "Subsurface Contamination Remediation: Accomplishments of the Environmental Management Science Program", ASC Symposium Series 904, Oxford University Press, 322-341, **2005** (INVITED BOOK CHAPTER)
- R. S. Addleman, O. B. Egorov, M. J. O'Hara, B. Busche, T. S. Zemanian, G. Fryxell "Preconcentration and Assay of Radionuclides with Self Assembled Monolayers on Mesoporous Supports"; *J. Radioanal. Nucl. Chem.*, **2005**, Vol. 263, No. 1, 59-64.
- Addleman, R.S., O'Hara, M.J., Grate, J.W., Egorov, O.B., "Chemically Enhanced Alpha Energy Spectroscopy in Liquids", *J. Radioanal. Nucl. Chem.*, **2005**, Vol. 263, No. 2, 291-294.
- Addleman, R.S., Egorov, O.B O'Hara, M.J., Zemanian T. S., Fryxell. G., Kuenzi D.,, "Nanostructured Sorbents for Solid Phase Microextraction and Environmental Assay", in "Nanotechnology and the Environment: Applications and Implications" ASC Symposium Series 890, Oxford University Press, 186-193, **2005** (INVITED BOOK CHAPTER)

- Addleman, R.S., O'Hara, M.J., Marks, T., Grate, J.W., Egorov, O.B., "Direct Actinide Assay with Surface Passivated Silicon Diodes", *J. Radioanal. Nucl. Chem.*, **2005**, Vol. 263, No. 2, 295-300.
- Egorov, Oleg; O'Hara, Matthew J.; Hoyt, Andrea E.; Grate, Jay W. Development and characterization of chemically selective scintillation fibers for Tc-99 sensing in groundwater. Abstracts of Papers, 227th ACS National Meeting, Anaheim, CA, United States, March 28-April 1, 2004
- Grate, J.W. and O. Egorov, "Automated Radiochemical Separation, Analysis, and Sensing," in Handbook of Radioactivity Analysis, Elsevier, 2003, pp. 1129-1164.
- Egorov O.B., O'Hara, M.J., Addleman, S.R., Grate, J. W. "Automation of Radiochemical Analysis: From Groundwater Monitoring to Nuclear Waste Analysis" in "Radioanalytical Methods in Interdisciplinary Research: Fundamental to Cutting Edge Applications", ASC Symposium Series 868, Oxford University Press, 249-270, 2003
- Hughes, L. and DeVol, T.A., "On-line Gross Alpha Radiation Monitoring of Natural Waters with Extractive Scintillating Resins," *Nuclear Instruments and Methods in Physics Research (Section A)*, A505, 435-438 (2003).
- Ayaz, B and DeVol, T.A., "Application of MnO₂ Coated Scintillator and Extractive Scintillating Resin to Screening for Radioactivity in Groundwater," *Nuclear Instruments and Methods in Physics Research (Section A)*, A505, 458-461 (2003).
- Tan, H., and DeVol, T. A., "Monte Carlo Modeling of Heterogeneous Scintillation Flow-Cell Detectors," *Nuclear Instruments and Methods in Physics (Section A)*, A515, 624-633 (2003).
- Roane, J.E. and DeVol, T.A., "Evaluation of an Extractive Scintillation Medium for the Detection of Uranium in Water," *Journal of Radioanalytical and Nuclear Chemistry* Vol. 263, No. 1, 51-57 (2005) Fjeld R.A., DeVol T.A., and Leyba, J.D., "Measurement of Radionuclides Using Ion Chromatography and On-Line Radiation Detection," (accepted for publication in the *Journal of Radioanalytical and Nuclear Chemistry*) (2004).
- Hughes, L.D. and DeVol, T.A., "Teflon coated PIPS detector flow cell for monitoring of ⁹⁹Tc in groundwater," *J. Radioanal. Nuc. Chem.* 2005 in press